Appendix 5

Phytoremediation

The presence of vegetation can have various effects on contaminants in soil or water. Studies indicate that vegetated soils are capable of more effective degradation, removal, and mineralization of total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs), pesticides, chlorinated solvents, and surfactants than are nonvegetated soils (US EPA, 2000). Certain plant roots can absorb or immobilize metal pollutants including cadmium, copper, nickel, zinc, lead, and chromium, while other plant species are capable of metabolizing or accumulating organic and nutrient contaminants. An intricate and complex set of relationships and interactions between plants, microbes, soils, and contaminants make these various phytoremediation processes possible.

The term phytoremediation is a combination of the Greek prefix *phyto*, for plant, and the Latin root *remidium*, "to correct or remove an evil". Defined, phytoremediation is the utilization of vascular plants, algae, and fungi to control, break down, or remove wastes, or to encourage degradation of contaminants in the rhizosphere, or root region of the plant (McCutcheon & Schnoor, 2003). Phytoremediation processes are most effective where contaminants are present at low to medium levels, as high contaminant levels can inhibit plant and microbial growth and activity (US EPA, 2000).

Metals, organics, and inorganic contaminants in stormwater and soils can be subject to:

- Degradation.
- Extraction by the plant.
- Containment within the plant.
- A combination of these mechanisms.

Plant processes that promote the removal of contaminants from soil and water are either direct or indirect. Direct processes include plant uptake into roots or shoots and transformation, storage, or transpiration of the contaminant (Hutchinson et al., 2003). Indirect plant processing involves the degradation of contaminants by microbial, soil, and root interactions within the rhizosphere (Hutchinson).

1. Degradation *(rhizodegradation, phytodegradation, phytovolatilization)*

Table 1 Phytoremediation processes contributing to degradation or transformation of contaminants in soil and water.

Type	Process	Appropriate contaminants
Rhizodegradation (Plant-assisted bioremediation, phytostimulation)	Plant exudates and other processes enhance soil bacterial growth, spur degradation by mycorrhizal fungi and microbes, and add aeration channels and oxygen to soils	Petroleum hydrocarbons, BTEX, PAHs, PCP, perchlorate, pesticides, PCBs and other organic compounds
Phytodegradation	Aquatic and terrestrial plants take up, store and biochemically degrade or transform organic compounds	Chlorinated solvents, methyl bromide, atrazine, DDT, tetrabromoethene, tetrachloroethane, dichloroethene, Cl and P-based pesticides, PCBs, phenols, anilines, nitriles, nutrients
Phytovolatilization	Plants take up volatile metals and organic compounds and transpire or diffuse contaminant or modified form of contaminant out of roots, leaves or stems	Arsenic, tritium, Se, mercury, m-xylene, chlororbenzene, tetrachloromethane, trichloromethane, trichloroethane, and other chlorinated solvents

(Adapted from information in US EPA, 2000)

The rhizosphere, or area of soil 1 mm from the plant root, is a dynamic and intricately complex environment (Olson et al., 2003). Increased microbial activity and biomass in this area of plant-microbe interaction has become recognized as the “rhizosphere effect” and is critical for rhizosphere bioremediation to take place (Olson et al.). Plant roots exude enzymes and other organic substances. These releases dramatically enhance microbial numbers and metabolic activity, and increase contaminant degradation and the availability of substances for uptake by the roots (Christensen-Kirsh, 1996). The process of breaking down an organic contaminant in soils through active microbial behavior enhanced by the rhizosphere is known as *rhizodegradation* (McCutcheon & Schnoor, 2003).

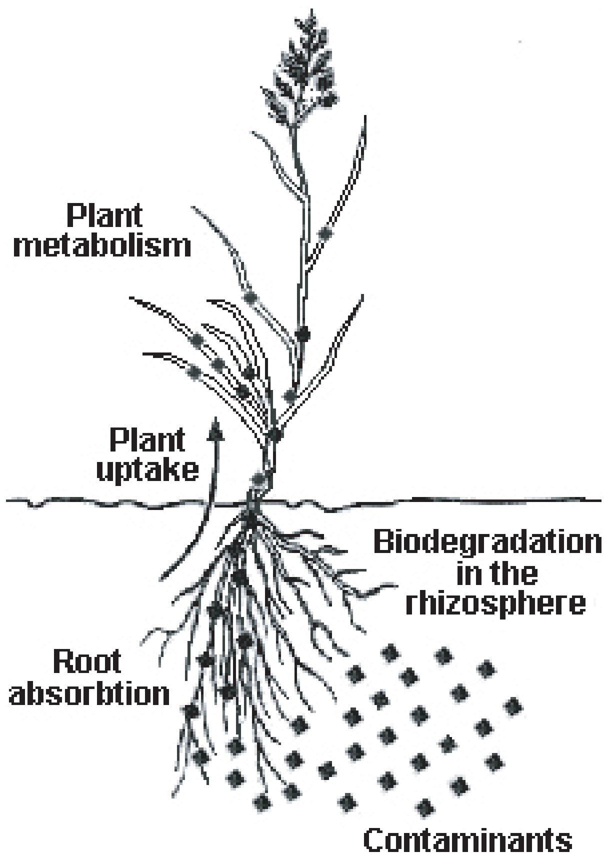

Figure 1 Illustration of basic phytoremediation pathways

The amount and type of compounds released into the soil, and the rhizosphere impacts on associated microbial communities, are specific to plant species (Olson et al., 2003). A synergistic relationship that promotes the exchange of water and nutrients is often established between plant roots and specialized soil fungi or mycorrhizae. This relationship also enhances plant growth (Banks et al., 2000).

Though plants are generally not capable of actually taking in and utilizing highly absorbed contaminants, such as PAHs, the presence of vegetation has been shown to accelerate the degradation of hydrocarbons by enhancing microbial activity (Banks et al., 2000). Root systems can encourage microbial degradation of large molecular organic contaminants (such as PAHs) that tend to bind to soil particles by activating otherwise dormant areas in the soil (Hutchinson et al., 2003). In some instances, the exuded enzymes are capable of detoxifying organic compounds without microbial assistance, a process known as *phytodegradation* (McCutcheon & Schnoor, 2003).

Plants transform certain contaminants through oxidation and reduction reactions, a conjugation phase (foreign compound joined by a plant sugar amino acid, thisol, or glutathione molecule), and deposition of the conjugates into vacuoles and cell walls (Dzantor & Beauchamp, 2002; Subramanian & Shanks, 2003).

The availability of a contaminant for uptake and transformation is also dependant upon the age of the contaminant and certainly the plant species (US EPA, 2000). This process of breaking down contaminants by plant metabolic activity is referred to as phytodegradation or *phytotransformation;* these terms can also apply to the breakdown of contaminants outside the plant through the release of enzymes produced by the plant and which result in the transformation of the compound (US EPA, 2000).

2. Extraction *(phytoextraction/phytomining, rhizofiltration, phytovolatilization)*

Table 2 Processes involving plant uptake or extraction of contaminants from soils or water.

Type	Process	Appropriate Contaminants
Phytoextraction (Phytomining)	Chemicals taken up with water by vegetation; harvested shoots could be smelted or metals otherwise extracted	Metals, metalloids, radionuclides, perchlorate, BTEX, PCP, organic chemicals not tightly bound to soil particles
Rhizofiltration	Contaminants taken up, sorbed, or precipitated by roots and/or shoots; sorbed to fungi, algae and bacteria	Metals, radionuclides, organic chemicals, nitrate, ammonium, phosphate, and pathogens
Phytovolatilization	Plants take up volatile metals and organic compounds and transpire or diffuse out of roots, leaves or stems	Se, tritium, As, Hg, m-xylene, chlororbenzene, tetrachloromethane, trichloromethane, trichloroethane, and other chlorinated solvents

(Adapted from information in US EPA, 2000)

Depending on the plant type and the contaminant, direct uptake can be considered either a passive and/or an active process (Chiou, 2002). The principal process is passive transport, with the primary transport medium, external water and soil water, carrying the contaminant into the plant. Active transport requires the plant to expend energy and generally applies to nutrients and other organic and inorganic ions required and extracted by the plant (Chiou).

Plants actually need metals, such as zinc and copper, as well as nutrients, to grow. When soil surrounding plant roots is deficient in essential elements, plants will exhibit symptoms indicative of deficiency (loss of leaf color, withering, dead spots, etc.) (Stern, 2000). Some plants, however, referred to as hyperaccumulators, make no distinction between heavy metals (such as cadmium or selenium) and those metals nutritionally necessary for growth (Raskin & Ensley, 2000; Stern). These plants absorb the metals through the root structure and store them in cell vacuoles, where tissues have been measured to contain 1,000 to 10,000 ppm of various heavy metals (Stern).

Potentially hazardous metals present in stormwater, such as zinc, copper, cadmium, and lead, can be absorbed by both terrestrial and aquatic plant roots as well as the shoots of submersed plants (Fritoff & Greger, 2003). The retention time and interactions with other elements in the water affect the bioavailablity of metals within a vegetated system exposed to stormwater (Fritoff & Greger). Metals may be contained by physical sequestration or accumulation in roots of non-harvestable plants.

The most important component of extractive phytoremediation is the availability of the compound (Dzantor & Beauchamp, 2002). The lipophilicity (fat-solubility), or distribution of a chemical from the soil solution to the lipids in the plant cell, is the primary controlling factor in the ability of plants to absorb and translocate organic chemicals (Hutchinson et al., 2003). Once transported into the plant cells, the chemical can be metabolized in a process very similar to mammalian metabolism; thus plants utilizing this process are frequently referred to as “green livers” (Dzantor & Beauchamp).

Using a process called *phytovolatilization,* elemental contaminants can be taken up, transformed to a volatile form, and transpired through roots, stems, or leaves (Doucette, Bugbee, Smith, Pajak, & Ginn, 2003). Selenium, for example, can be transformed into volatile dimethyl selenide, not known to represent any health risk once transported through air. Volatile organic compounds can be taken up and directly transpired or diffused through roots, stems, and foliage (Doucette et al.). Application or use of phytovolatilization requires a thorough examination of potential health risks associated with air transport of the contaminant or modified form of the contaminant in the atmosphere.

3. Containment/Immobilization *(phytostabilization, rhizofiltration)*

Table 3 Immobilization or containment processes preventing contaminant movement, leaching or transport.

Type	Process	Appropriate Contaminants
Phytostabilization	Vegetation prevents erosion and sorbed contaminant transport; often involves revegetating an area where natural vegetation cannot be sustained due to high contaminant concentrations	Metals, phenols, tetrachloromethane, trichloromethane, and other chlorinated solvents
Rhizofiltration	Contaminants taken up, sorbed, or precipitated by roots and/or shoots; sorbed to fungi, algae and bacteria	Metals, radionuclides, organic chemicals, nitrate, ammonium, phosphate, and pathogens

(Adapted from information in US EPA, 2000)

Root and microbial interactions can immobilize organic and some inorganic contaminants by binding them to soil particles and, as a result, reduce migration of the contaminant to groundwater (Christensen-Kirsh, 1996). The process of holding contaminated soils in place with vegetation, minimizing disturbance of contaminants bound to soil particles, and preventing contaminant movement is referred to as **phytostabilization** (McCutcheon & Schnoor, 2003).

The process where heavy metal contaminants in water are absorbed or precipitated onto or into plant roots is referred to as **rhizofiltration**. The plant may or may not actually take in and translocate the contaminant. The contaminant can be contained, immobilized or accumulated within or on the root structure. Generally this application is associated with contaminants carried in water rather than contaminated soil particles (US EPA, 2000). This process is heavily dependant on pH levels of the solution and harvesting of plants used in this process will often be necessary to reduce the reintroduction of the contaminant into soils or water.

Plant Selection Considerations

Use of native plant species for phytoremediation is generally favored; natives require less maintenance and present fewer environmental and human risks than do non-native or genetically altered species. Non-native species that require fertilizers or large amounts of irrigation will contribute to, rather than reduce, negative effects of stormwater runoff. Properly selected native plant communities are most tolerant of soils, climatic conditions, and seasonal cycles of inundation and drought. However, particular non-native plants may work best in remediation of a specific contaminant and can be safely used under circumstances where the possibility of invasive behavior has been eliminated (US EPA, 2000).

Scientific studies using phytoremediation techniques have focused almost entirely on monoculture trials, while ecosystem and plant community uses and effects remain largely unexplored. The drawbacks of phytoremediation efforts relying on monocultures are increased susceptibility to disease and other natural events damaging the plants, as well as reduced ecological diversity and wildlife habitat benefits (Marmiroli & McCutcheon, 2003).

Limiting Conditions

The primary factors that limit the effectiveness of phytoremediation are climate conditions, particularly temperature, and contaminant exposure to the plant root zone. In temperate regions, dormant periods for many plants that coincide with high precipitation periods may limit contaminant uptake during periods when pollutant loads are potentially largest (Christensen-Kirsh, 1996). Effective phytoremediation requires that root systems extend into the contaminated region or that the contaminants be brought within range of the rhizosphere (US EPA, 2000).

Microbial populations and their level of activity are strongly influenced by soil pH levels and water availability. Most biological activity occurs in soils with pH levels between 5 and 10 (Hutchinson et al., 2003). Low pH levels are optimal for metal availability, but can have adverse effects on vegetation. Microbial activity is maximized when 60 percent of soil pore space is filled with water. Activity is nearly absent with low water availability. Saturated soils have limited available oxygen, forcing a decline in microbial activity (Hutchinson et al.).

The physical characteristics of soil, such as percentages of clay and/or sand, can alter the availability of oxygen, nutrients, and water for plant and microbial use. Soils with high clay content, for example, have lower hydraulic conductivity and diffusion coefficients, and can render contaminants unavailable to microorganisms. The presence of vegetation can promote the development of soil structure, increase microbial activity within the rhizosphere, and, as a result, enhance the transport of water, nutrients, and contaminants through the soils system (Hutchinson et al., 2003). Adding organic amendments, such as compost, to disturbed urban soils can increase plant root growth, improve water-holding capacity of the soil, and encourage a wide variety of soil organisms.

The importance of optimizing the productivity and interactions between plants and microbes cannot be overstated, and the success of most phytoremediation applications (volatilization, extraction, stabilization, transformation, phytodegradation and rhizodegradation) will be largely dependant on this dynamic relationship (Olson et al., 2003).

Phytoremediation efforts can also be influenced by the presence of multiple contaminants, which, in combination, can inhibit pollutant processing. Understanding which contaminants are present is necessary to inform decisions regarding appropriate plant and soil selection (Dzantor & Beauchamp, 2002).

Concerns and Considerations

Utilization of some phytoremediation techniques, such as the extraction and sequestration of heavy metals in plant tissues, may require harvesting and proper disposal or recycling of contaminated vegetation. Most phytoremediative plants, however, do not accumulate significant levels of contamination and do not require specific treatment or disposal (US EPA, 2000). Existing natural vegetation on sites receiving stormwater runoff likely extract, metabolize, and/or degrade many contaminants (US EPA, 2000). However, the complexity of interactions between variables, such as plant communities, climatic conditions, soils, and combinations of contaminants will undoubtedly prohibit a comprehensive understanding of all interactions at every site for some time to come.

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